# Thermally Processed Keratin Films

**Justin R. Barone, Walter F. Schmidt, Christina F. E. Liebner**

*USDA/ARS/ANRI/EQL Beltsville, Maryland 20705*

Received 4 May 2004; accepted 27 December 2004
DOI 10.1002/app.21901
Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Keratin obtained from poultry feathers was modified with glycerol, which acted as a plasticizer. Films were prepared by pressing the modified keratin at temperatures concurrent with typical polymer processing temperatures. The films were completely cohesive as opposed to partially cohesive if pressed under the same conditions without glycerol. The films were "tough" and the mechanical properties show similarities to the properties of commercially available commodity thermoplastics. The keratin films were produced in a few minutes without reducing or oxidizing agents. The keratin films could have potential applications for which environmentally friendly materials are needed, such as food packaging or mulching films. © 2005 Wiley Periodicals, Inc.* J Appl Polym Sci 97: 1644–1651, 2005

**Key words:** biopolymers; proteins; mechanical properties; differential scanning calorimetry; NMR

## INTRODUCTION

Recently, there has been interest in developing biopolymer materials for many different applications. Biopolymers, whether natural or synthetic, are biocompatible and therefore appropriate for biomedical applications such as implantation or drug delivery. In addition, biopolymers are being considered as alternatives to commodity synthetic polymers because the biopolymers are biodegradable or environmentally friendly. Biopolymers from sustainable resources would have a distinct advantage over petroleum-derived polymers in this respect. Naturally derived proteins from gelatin,[1] soybean,[2–4] wheat,[5–8] sunflower,[9–11] corn,[12–18] fish,[19] milk,[20,21] wool,[22] and poultry feather[23,24] have been processed into films using a variety of techniques. These techniques include solvent-cast and thermally processed films. Solvent casting is tedious and, if the solvents are volatiles, would defeat the purpose of environmental friendliness. Thermal processing is simpler and the method is currently used in industry. If biopolymers from sustainable resources are to be used commercially, the biopolymers have to be processed through preferred processing methods. It becomes imperative to identify biopolymers from sustainable resources that can be easily processed using available technology.

Keratin can be found in hair, nail, epidermis, hoof, horn, and feather and is a unique protein because it contains a large amount of the amino acid cysteine compared to other proteins.[25,26] Cysteine (C) is a sulfur-containing amino acid and can form sulfur–sulfur (S–S) cystine bonds with other intra- or intermolecular cysteine molecules. Intermolecular cystine bonds are referred to as "crosslinks." The crosslinks plus other protein structural features, such as crystallinity and hydrogen-bonding, give keratin high strength and stiffness.[27] The amount of cysteine varies depending on the keratin source. Wool keratin contains 11 to 17% cysteine while feather keratin contains about 7% cysteine.[26,28]

Each year, the U.S. poultry industry discards ~2.5 billion pounds of dry chicken feathers.[29] In addition to feathers, the feather waste contains fat, water, and soluble protein. Some of the waste can be autoclaved and turned into a low-value animal feed. The rest must be disposed of and creates a large waste problem for the poultry industry. The USDA has developed a process to efficiently and cost-effectively clean the feather waste to obtain pure feather.[30] The process can further separate the feather into fiber and quill fractions. Raman spectroscopy shows that the feather fiber has 41% $\alpha$-helix and 38% $\beta$-sheet protein structures, with the balance being disordered structures.[31]

Most studies on processing keratin focus on reducing, or breaking, covalent sulfur–sulfur bonds to obtain a soluble fraction.[23,24] Reduction schemes require multiple chemical treatment steps, sufficient time for reaction, and subsequent processing to eliminate the

*Correspondence to:* J. R. Barone (baronej@ba.usda.gov).

Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

Journal of Applied Polymer Science, Vol. 97, 1644–1651 (2005)
© 2005 Wiley Periodicals, Inc. *This article is a US Government work and, as such, is in the public domain in the United States of America.

chemicals used for treatment. Therefore, reduction of even small amounts of keratin proceeds on the order of hours to days.

Reduction of all of the sulfur–sulfur bonds and subsequent solubilization of the keratin will allow for a reasonable determination of the keratin molecular weight. Feather keratin has a molecular weight of about 10,500 g/mol, which corresponds to about 90 amino acids.[32] The reduced keratin has been dissolved in solvent and used to cast cohesive films for agricultural and food packaging applications[2,24] and as a protein substrate for cell culturing.[33] The advantages of using a biologically derived polymer like a protein over a synthetic polymer in these applications are obvious. Formulations containing natural and biodegradable proteins are a great food packaging system assuming the mechanical properties and permeability are suitable. For cell culturing, cells are receptive to certain amino acid sequences so protein substrates are preferred and proteins are more biocompatible than synthetic polymers. Yamauchi et al. [22] produced films from wool with modulus, stress at break, and strain at break values of 2.5 MPa, 0.25 MPa, and 32%, respectively, at 65% relative humidity. Okamoto and Setagaya-ku[2] reported stress at break values for pure keratin films made from chicken feather of 6 MPa with a strain at break of about 140%. Reduced keratin films that contained glycerol made by Schrooyen et al.[24] had modulus values of 350 MPa, stress at break values of 15–25 MPa, and strain at break values of 10–50% depending on cysteine modification.

Proteins are temperature sensitive and require thermal processing at reduced temperatures. The use of plasticizers can lower thermal transition temperatures to acceptable levels. Proteins contain a fair amount of hydrogen-bound water, which will typically associate with the –OH groups in proteins. The bound water associates with other protein or water molecules and stabilizes the protein structure.[34] Loss of that water at high temperatures will destabilize the protein structure and cause a rearrangement.[35] Proteins from soy,[3] wheat,[6,8] sunflower,[9–11] corn,[14,15,18] fish,[19] and milk[20] have been thermally processed into films using a variety of techniques but always with a low molecular weight plasticizer such as glycerol, polyethylene glycol, propylene glycol, or sorbitol.

In this article, natural keratin from the fiber fraction of poultry feather was blended with various amounts of glycerol. No reduction or oxidation agents were used in the process. The keratin/glycerol blend was then pressed into films at typical polymer processing temperatures. Semitransparent, cohesive films were easily obtained. The films were tested in uniaxial tension to assess mechanical properties. DSC and NMR showed how the molecular structure of the keratin changed as a function of the processing condition.

## EXPERIMENTAL

### Feather keratin

Keratin feather fiber was obtained from Featherfiber® Corp. (Nixa, MO). Feather fiber is semicrystalline and has a relatively constant diameter of approximately 5 $\mu$m with a density of 0.89 g/cm$^3$.[36]

Feather fiber of 0.0053 cm length was made by grinding the fiber on a Retsch PM 400 ball mill. Feather fiber was loaded into 500-mL stainless-steel grinding vessels so that it occupied about a quarter of the volume. The grinding media was four 40-mm stainless-steel spheres for a total of 1,132 g grinding media. Grinding proceeded at 200 rpm for 30 min. This resulted in a feather fiber "powder." The ground feather fiber was sieved by hand through a sieving stack with hole sizes from 0.1 to 0.0038 cm. Vigorously shaking the stack for more than 15 min produced the desired fiber fraction. The fraction used went through the 0.0075-cm sieve but not the 0.0053-cm sieve.

### Film preparation

Glycerol (mol. wt. = 92.1 g/mol, boiling point = 290°C, density = 1.26 g/cm$^3$) was added to keratin from 15 to 80 wt %. Mixing occurred on a Brabender mixing head. First, the fibers were added into the mixing head and then the glycerol was slowly added. Mixing proceeded at 40°C and 50 rpm for 40 min. The total material occupied 70% of the volume of the mixer.

Following mixing, 5 g of sample was sandwiched between aluminum foil and pressed into films in a Carver Press Autofour/30 Model 4394 at 160°C, 88,964*N* for 2 to 8 min. The film was removed and allowed to air cool until it reached room temperature. The resulting film diameter and thickness varied depending on glycerol content. The diameter of the films ranged from ~8 to 12 cm for the 15 and 50 wt % glycerol films, respectively. The thickness of the films ranged from 0.10 cm for the 15 wt % glycerol to 0.04 cm for the 50 wt % glycerol. Therefore, the applied stress was about 16 to 7 MPa for the 15 wt % glycerol and 50 wt % glycerol films, respectively. As a control, pure feather keratin fiber was also pressed at 160°C and 16 MPa for 2 min. However, this film was only used for moisture absorption and DSC experiments. The film was too brittle to extract tensile testing samples. It was not possible to press cohesive films from the material when the glycerol content was greater than 50 wt %.

Samples for testing were cut from the films using a pair of surgical scissors. The sample size was the ASTM D638 Type IV dogbone sample reduced to 75% of the recommended size.

### Mechanical testing of films

Mechanical testing of the dogbone films was performed at various times after sample preparation. For the studies on pressing time and glycerol content, films were tested immediately after sample preparation, i.e., within 20 min of film pressing. For the study on glycerol loss and water exposure, samples were tested after the described time. Uniaxial tensile testing was performed using a Com-Ten Industries 95 RC Test System. The distance between the grips was 1.96 cm and the applied test speed was either 2.54 or 12.7 cm/min. A minimum of three films for each condition was tested at room temperature and humidity.

### DSC of films

The effect of glycerol and thermal processing was assessed using a TA Instruments 910s DSC. Only one heating cycle was employed. The DSC analysis proceeded from 30 to 320°C at a heating rate of 10°C/min according to ASTM D3417. The assignment of peaks and integration of peak areas was performed according to ASTM D3418.

### Solid-state $^{13}$C-NMR

Spectra were collected on a Bruker DMX-400 NMR Spectrometer at a field strength of 9.4 T. Samples were spun at 5 kHz in ceramic rotors inside a Bruker MAS probe with magic angle spinning. Spectra were obtained with a 1-ms contact time, a 2-s recycle time, and a 1,000-W decoupler power. The $^{13}$C spectra were recorded at 100.63 MHz typically at a spectral width of 26,000 Hz, 16k data points, 2k scans, and line broadening of 16 Hz. Adamantine was the external intermediate reference standard used to set the relative chemical shift scale.

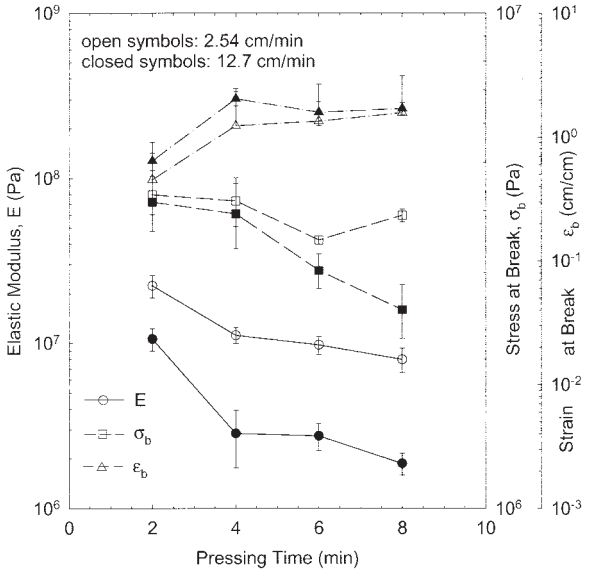



**Figure 1** Effect of pressing time on physical properties for films made from 50 : 50 wt % keratin : glycerol pressed at 160°C and 7 MPa. Test speeds were 2.54 and 12.7 cm/min.

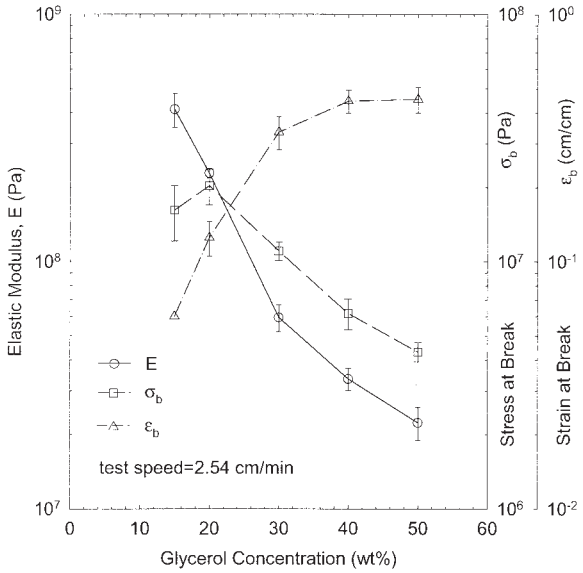



**Figure 2** Effect of glycerol concentration on films pressed for 2 min at 160°C. Test speed was 2.54 cm/min.

## RESULTS AND DISCUSSION

### Effect of pressing time

Figure 1 shows the effect of pressing time on the physical properties for 50 : 50 wt % glycerol : keratin feather fiber films pressed at 160°C and 7 MPa. The modulus, $E$, decreased as the films were pressed for longer periods of time. The stress at break, $\sigma_b$, decreased slightly at higher pressing times. Increasing pressing time increased strain at break, $\varepsilon_b$. In other words, the films became more ductile as the films were pressed for longer periods of time. The films pressed for 4 min or more failed at over 100% strain. The modulus had the greatest dependence on applied testing speed, which demonstrated the nonlinear viscoelastic nature of the films.

### Effect of glycerol concentration

Figure 2 shows the dependence of the film physical properties on glycerol content. The films were pressed at 160°C for 2 min. As expected, the keratin films became more ductile with the addition of glycerol. However, there was a limiting amount of glycerol that could be added. Films with greater than 50 wt % glycerol were very incomplete after pressing, i.e., the films contained "holes." Reduction of the pressing force or time did not result in a cohesive film. At 15 wt % glycerol, the films appeared to fail at defects in

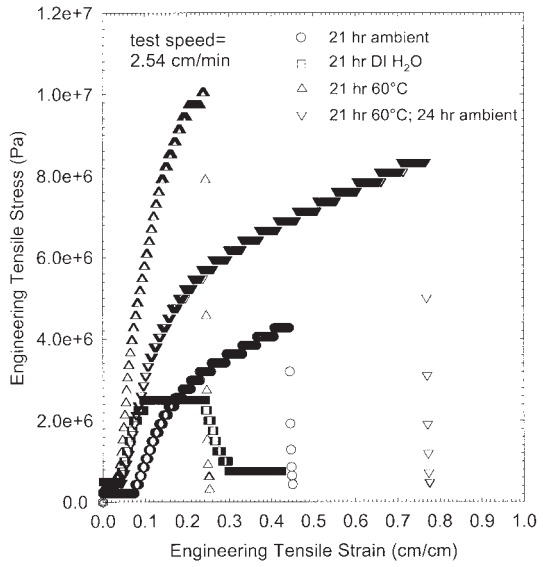



**Figure 3** Effect of film treatment on 50 : 50 wt % keratin : glycerol films pressed for 2 min at 160°C and 7 MPa. Test speed was 2.54 cm/min.

the structure resulting in the lower stress at break values. Visual inspection of the 15 wt % glycerol films showed vestiges of the original fibers that had not been pressed, resulting in defects in the film. When the glycerol content was greater than 20 wt %, some glycerol began to diffuse out of the films after about 12 h at room temperature.

The pressed films that contained no glycerol were too brittle to obtain good dogbones for testing. However, if the modulus curve in Figure 2 is extrapolated to 0 wt % glycerol, a modulus value of about 3 GPa is obtained. This is interesting because the mechanical properties of whole feathers and feather rachis (i.e., the quill or shaft of the feather) have been measured for several species of birds and have produced similar modulus values. Purslow and Vincent[37] measured the elastic modulus of dehydrated primary feather shafts from pigeons and obtained modulus values of 7.75–10 GPa. Fraser and MacRae[27] reported modulus values for Laysan albatross feather of 5.2 and 3.4 GPa at 65 and 100% relative humidity, respectively. More recently, Bonser and Purslow[38] measured the modulus of the feather shaft from a variety of birds and found an average value of 2.5 GPa at room temperature and humidity. Cameron et al.[39] showed that the modulus of feather shaft keratin is 2.5–5 GPa for swan and goose feather whereas ostrich feather shaft keratin had a modulus value of about 1.5 GPa, all at 50% humidity.

### Effect of film environment

Figure 3 shows representative engineering stress–strain curves for 50 : 50 wt % keratin feather fiber/glycerol films treated several different ways. Multiple samples were tested for each and all exhibit similar behavior to the curves shown for each condition. All of the samples were pressed and then held: (a) at ambient conditions for 21 h, (b) in deionized water (DI $H_2O$) for 21 h, (c) in a convection oven at 60°C for 21 h, (d) in a convection oven at 60°C for 21 h followed by ambient conditions for 24 h. After each treatment, any glycerol or water on the films was wiped off. Soaking the films in deionized water resulted in a similar modulus as the film held at ambient conditions, but there was lower stress and strain at break. So, water exchanges with the glycerol in the keratin structure. The glycerol added ductility and cohesivity to the film. Holding the film at 60°C resulted in a large increase in modulus and stress at break over the film held at ambient conditions for the same period of time. However, the film treated at 60°C had a lower strain at break. DSC showed a shift in the melting point from 241 to 248°C for films right after pressing and after 21 h at 60°C, respectively. For these films, the annealing at 60°C resulted in a modification of the crystal structure and a concurrent increase in the modulus and stress at break. But some loss of glycerol made the film more brittle. Allowing this film to rehydrate by holding at ambient conditions for 24 h after annealing decreased modulus and stress at break slightly but increased strain at break several times. This showed that the film properties were optimized when the keratin was allowed to absorb water from the atmosphere to an equilibrium value.

### Loss of glycerol

Figure 4 shows a plot of the normalized mass of keratin/glycerol films as a function of time. In Figure 4, the mass of the films over time, $m$, was normalized by the original mass of each film, $m_0$. Initially, all of the films gained mass immediately after pressing ($m/m_0 > 1$). This was a slight rehydration of the films. For 0 to 20 wt % glycerol, the films absorbed about 3% by weight of water from the atmosphere to reach equilibrium. However, for glycerol contents higher than 20 wt %, the glycerol began to diffuse out of the film. Two $m/m_0$ values at a given time show the removal of the glycerol from the surface of the film by wiping. The curves should theoretically approach the original mass of keratin in the film if all of the glycerol was lost. However, some of the glycerol was retained as desorption stops after about 500 h and the limiting value of the keratin weight fraction was not reached.

For the films with greater than 20 wt % glycerol, the films seemed to retain about $m/m_0 = 0.2–0.3$ of glycerol. For example, the 30, 40, and 50 wt % glycerol films reached equilibrium at $m/m_0 = 0.91$, 0.82, and 0.78, respectively, which corresponded to $m/m_0 = 0.21$, 0.22, and 0.28 retention of glycerol. The amino

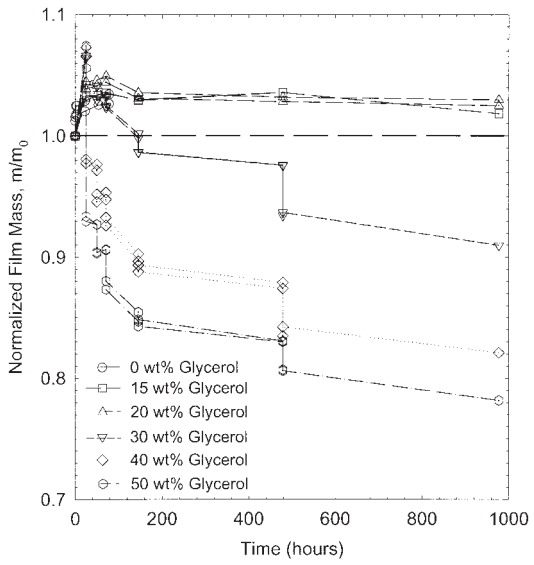



**Figure 4** Normalized film mass as a function of time. Periodically the film surfaces were wiped clean and weighed showing glycerol loss and water absorption.

acid sequence of feather keratin reveals that there are 22% –OH-containing amino acids (serine, S = 17%, threonine, T = 4%, tyrosine, Y = 1%).[28] So, the mass fraction of bound glycerol remaining in the film approaches 22%:

$$\frac{m_{g,b}}{m_{m,b} + m_k} \rightarrow 0.22$$

where $m$ is mass, g is glycerol, b denotes "bound," and k is keratin. So the glycerol may associate with the –OH-containing amino acids in keratin. This is investigated further with DSC and NMR.

### Keratin structural changes

DSC was used to study structural changes in the feather keratin as a function of thermal processing and glycerol concentration. Figure 5 shows the results for four feather keratin samples: (a) the original fiber material subsequent to grinding but prior to pressing (black); (b) the fiber simply pressed at 160°C and 16 MPa for 2 min (red); (c) a film that originally contained 50 wt % glycerol but the excess was allowed to diffuse out, so 28 wt % glycerol remained (green); (d) a film that originally contained 50 wt % glycerol but all of the glycerol had been removed by soaking in water (blue). The original feather keratin fiber had two peaks, a low temperature peak around 110°C associated with the amount of hydrogen-bound water in the keratin (sometimes referred to as the denaturation peak) and a higher temperature peak around 230–240°C corresponding to the crystalline melting temperature of the keratin. The crystalline melting peak was broad, indicating that there was a distribution of crystal sizes. There were some peaks higher than 240°C and the baseline began to drift and this was associated with the thermal degradation of the keratin. Visual observation also showed that the keratin changed color to black and emitted an odor at these high temperatures. Pressing the keratin on the compression molder at 160°C significantly reduced the area under the low temperature peak, indicating water was lost, and the melting peak sharpened and shifted to lower temperature, i.e., a sharper peak of lower intensity appeared at ~200°C.

For the film that still contained 28 wt % glycerol, the low temperature peak shifted to higher temperatures, ~130°C, higher than the original denaturation temperature of the protein. Glycerol has a boiling point of about 290°C. This indicated that the glycerol replaced water in keratin, enabling the keratin film formation. Glycerol, a hydrophilic molecule, would be soluble at the hydrophilic or –OH containing amino acids. So the DSC results correlated with the observed retention of glycerol. The sharp crystalline peak at 200°C was gone and the glycerol evaporated from the film at ~250°C. Finally, DSC was performed on a film after the glycerol had been removed. To remove glycerol, the film was weighed and then soaked in deionized water, removed periodically, dried, and reweighed. After about 24 h, all of the glycerol was gone. DSC showed that the low temperature peak reappeared at around 110°C. A small crystalline peak existed at 200°C and a broader crystalline peak occurred at 230–250°C. Therefore, glycerol disrupted the crystalline structure of the keratin, giving a less crystalline and more amorphous material that was easier to process.

To investigate this phenomenon further, NMR spectroscopy was performed on the films. Figure 6(a)

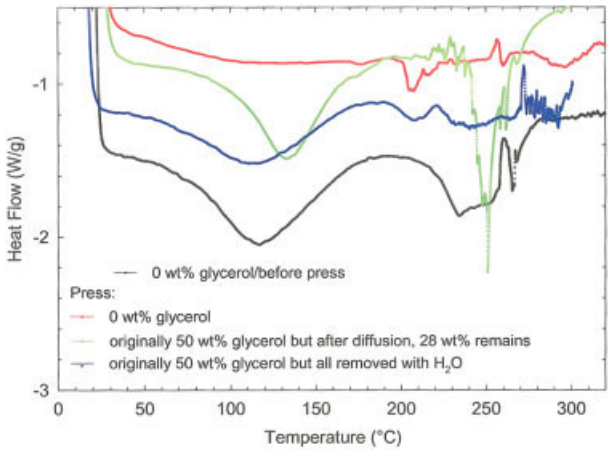



**Figure 5** DSC results for native feather keratin; pressed feather keratin; keratin : glycerol film after excess glycerol had diffused out, but 28 wt % glycerol remained in film; and keratin : glycerol film after removal of glycerol by soaking in water.

shows the solid-state $^{13}$C-NMR spectra for keratin feather fiber before and after pressing and for a film that once contained 30 wt % glycerol. The amino acid peaks proline (P, 11.5%), cysteine (C, 7.3%), leucine (L, 6.3%), valine (V, 9.4%), and glycine (G, 11.5%) are labeled in the figure.[40] Although some of the frequencies from these amino acids were in the protein overlap in the region between 0 and 40 ppm, the sharp portions of the peaks indicated that some of these amino acids were mobile. The broader portions of the peaks overlapping in the large peak indicated some of these amino acids were much more immobile, i.e., structured, whether it be through cystine bonding, hydrogen bonding, or crystallinity. The region of the broad peak at about 62 ppm was associated with the $CH_2$ group in serine, S (16.7%), and tyrosine, Y (1.0%), and with the CH group in threonine, T (4.2%), and contained overlapping contributions from all three. The peak at ~175 ppm was the carbonyl (C=O) peak with contributions from the protein backbone of each amino acid and from the side chains of multiple amino acids, i.e., aspartic acid, asparagines, glutamine, and glutamic acid. Hydrogen bonding between amino acids in the keratin structure occurred between C=O and N–H so the broad carbonyl peak indicates hydrogen bonding.

Upon pressing, the V, C, P, and L peaks all broaden. This was evidenced by the lower intensity of the visible portions of the peaks and the consumption of the rest of the peak into the large peak between 0 and 40 ppm. So the original molecular order was perturbed upon pressing. The fiber fraction contains $\alpha$-helix structure and the change in peaks may indicate a transition from $\alpha$-helix to $\beta$-sheet structure.[31,35] The change in the crystalline structure observed in DSC supports this conclusion. The spectrum did not differentiate whether the change in the cysteine peak was because of a change in structure from $\alpha$-helix to $\beta$-sheet or because of a loss of cystine bonds. After pressing at 160°C, water was lost from the protein, which meant that the water maintaining the structure was no longer present and the protein was rearranged. The relative intensity of the $CH_2$–OH region near 62 ppm increased after loss of water. This indicated that the S, T, and Y sites were no longer hydrogen bound to the water, which had stabilized the original protein structure. Further, the increased broadening of the carbonyl peak supported that the backbone of the protein as well as the side chains were perturbed by pressing, as would be expected from conversion of the original structure into a $\beta$-sheet.

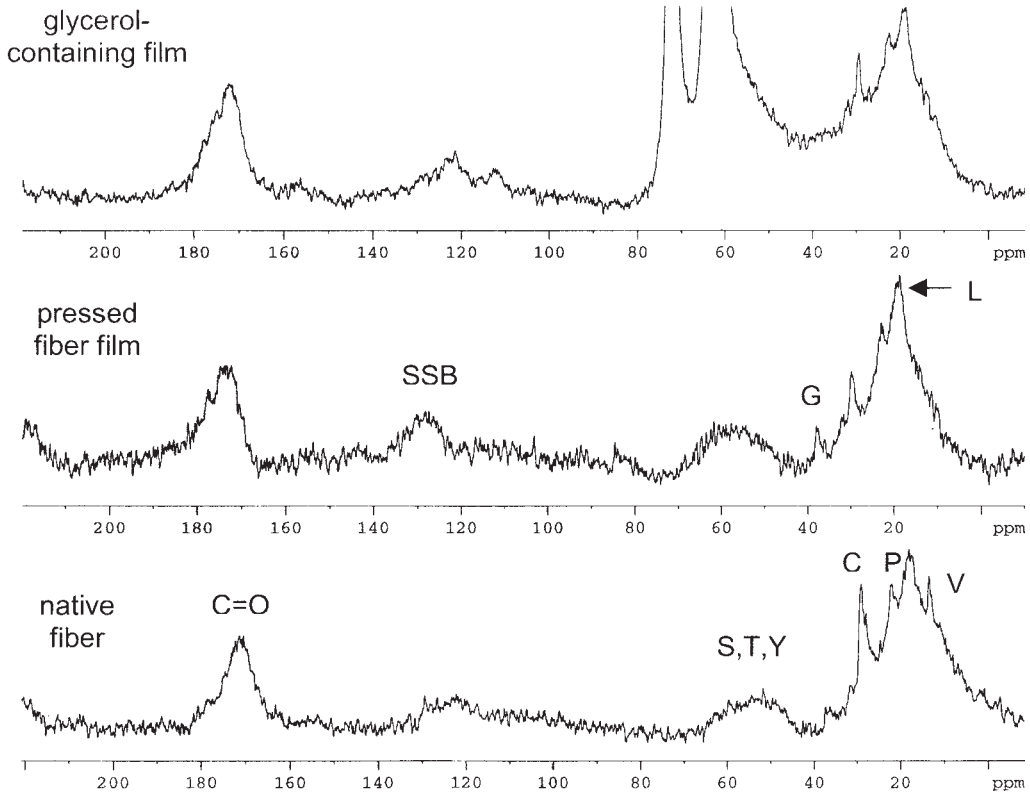
The addition of glycerol to keratin further changes the spectrum. The largest difference occurred at the serine peak. Glycerol appeared at the S, T, and Y sites as a large, broad peak. The peak was so broad that glycine was consumed in the $CH_2$–OH peak. Unlike water, glycerol persists in keratin at the processing temperature of 160°C. Figure 6(b) shows a close-up view of the NMR spectrum of glycerol and the –OH portion of the 30 wt % glycerol film spectra. The triplet at 62 ppm corresponded to the end $CH_2$–OH groups on the glycerol and the doublet at the 72-ppm peak corresponded to the middle CH–OH group on glycerol. In the solids probe glycerol spectrum, the sharp peaks occurred because the $CH_2$ and CH glycerol sites in a liquid environment were close in space primarily to the H atoms to which they were directly bound. When introduced into the keratin structure, the triplet and doublet became wide peaks. Now, the same glycerol sites were close in space to H atoms bound to protein structure in neighboring amino acids. Thus the glycerol was intimately bound to the protein at the molecular level and the keratin was not a suspension of solids in a liquid. The carbonyl peak in the glycerol film spectrum was relatively sharper than in the film without glycerol, indicating that the carbonyl groups were made more mobile by inclusion of the glycerol and therefore the protein more pliable upon pressing.

### Thoughts on the processability of feather keratin

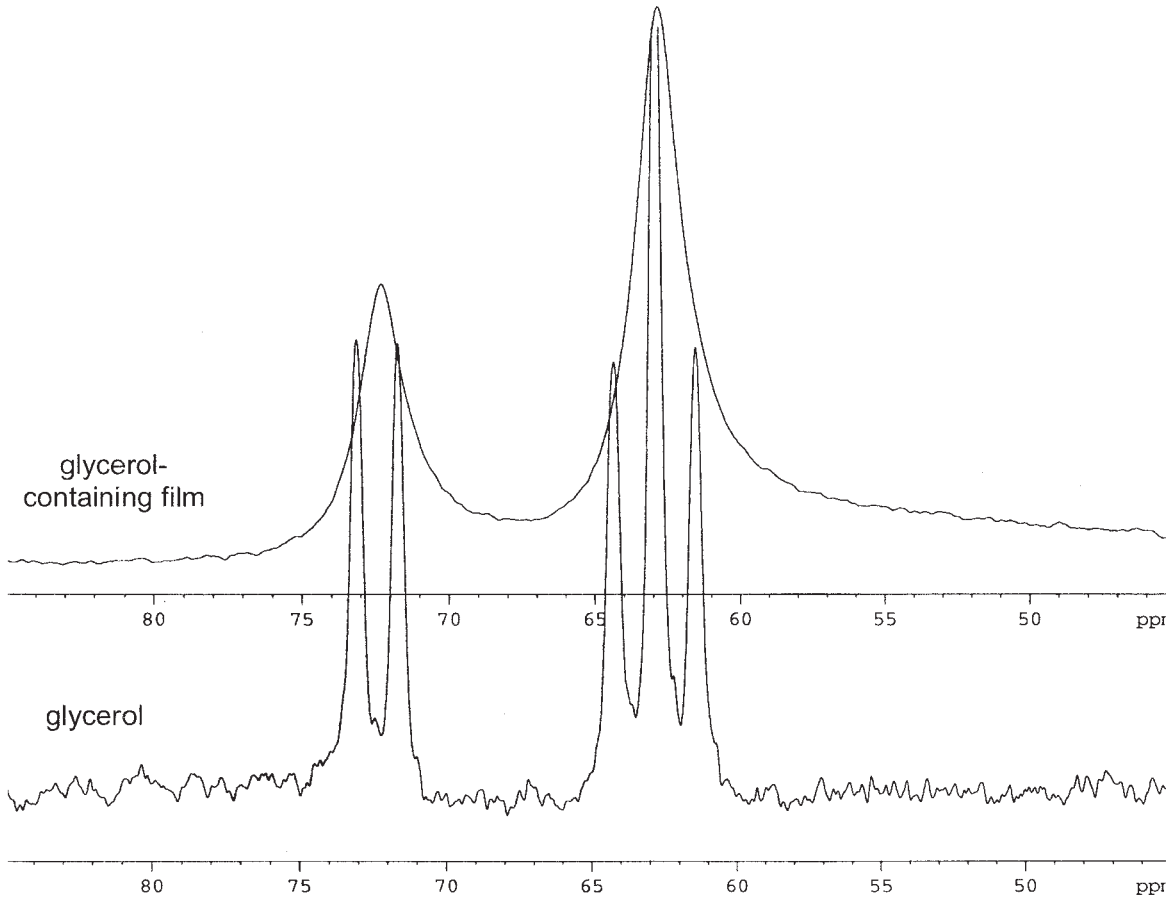
Generally, keratins are not believed to be processable by conventional thermal techniques because of the high amount of cysteine relative to other proteins. In other words, keratins are believed to be thermosetting polymers with a permanent network rather than thermoplastic polymers. Corn gluten meal is the protein fraction from corn and contains the proteins $\alpha_1$-zein, $\alpha_2$-zein, $\beta$-zein, and glutelin.[41] Wheat gluten is the protein fraction from wheat and contains the proteins gliadin and glutenin.[42] Whey protein isolate is the protein fraction from milk and contains the proteins $\alpha$-lactalbumin, $\beta$-lactoglobulin, and serum albumin.[27] All of these proteins contain cysteine and have been shown to be thermally processable in the presence of a suitable plasticizer. Wool keratin, feather keratin, $\beta$-zein, gliadin, glutenin, $\alpha$-lactalbumin, $\beta$-lactoglobulin, and serum albumin all contain more than 2% cysteine, which could theoretically result in a fully gelled network.[43]

However, wool keratin is not thermally processable. So, two possibilities arise. The first is that all of the C in wool is devoted to intermolecular cystine bonds whereas the other proteins have a mix of inter- and intramolecular cystine bonds. This then means that there is not a fully gelled network for the proteins other than wool but there are enough free chains to allow for plasticization and chain interdiffusion. So the intermolecular cystine bonds result only in a high-molecular-weight protein fraction.

The second possibility is that there is some similar network formation in all of the cysteine-containing proteins, but something about the amino acid composition of each is uniquely important to its physical




(a)




(b)

**Figure 6** (a) $^{13}$C-NMR spectra for native feather keratin, pressed feather keratin, and keratin : glycerol film, SSB is "spinning side band"; (b) close-up of $CH_2$–OH and CH–OH region of glycerol-containing film and glycerol on its own.

properties. It was shown here that the plasticizer associates with the S, T, and Y amino acids in the protein. This would indicate that these portions of the chain become the most mobile while the portions of the chain that contain C are the most immobile. So proteins that contain high amounts of –OH relative to cystine bonds would be more processable. For example, feather keratin has a serine, threonine, and tyrosine content of 22% and a cysteine content of 7% for a ratio of 3.1. Wool contains serine, threonine, and tyrosine at 20% and cysteine at 11% for a ratio of 1.8. In other words, there are three times as many mobile sites as immobile sites for feather keratin but only 1.8 times as many mobile sites over immobile sites for wool keratin.

## CONCLUSIONS

The results in this article show that it was easy to obtain cohesive films with good physical properties from poultry feather keratin. No reducing or oxidizing agents were needed and only standard polymer processing techniques were used. Glycerol associated with the –OH containing hydrophilic amino acids in keratin. Glycerol replaced water in the native keratin structure and acted as a plasticizer for the protein, introducing free volume into the polymer. The increased free volume did not allow keratin molecules to recrystallize after processing, resulting in a somewhat clear, amorphous film that could be stretched over 100%. Mobility in portions of the keratin molecule allowed those parts of the chain to interdiffuse with other mobile chain parts and a cohesive film to be obtained.

## References


1. Bigi, A.; Borghi, M.; Cojazzi, G.; Fichera, A. M.; Panzavolta, S.; Roveri, N. J Therm Anal Cal 2000, 61, 451.
2. Okamoto, S.; Setagaya-ku, T. Cereal Foods World 1978, 23, 256.
3. Vaz, C. M.; Mano, J. F.; Fossen, M.; van Tuil, R. F.; de Graaf, L. A.; Reis, R. L.; Cunha, A. M. J Macromol Sci Phys 2002 B41, 33.
4. Kim, K. M.; Marx, D. B.; Weller, C. L.; Hanna, M. A. J Am Oil Chem Soc 2003, 80, 71.
5. Mangavel, C.; Barbot, J.; Gueguen, J.; Popineau, Y. J Agric Food Chem 2003, 51, 1447.
6. Domenek, S.; Feuilloley, P.; Gratraud, J.; Morel, M-H. Guilbert, S. Chemosphere 2004, 54, 551.
7. Irissin-Mangata, J.; Baudin, G.; Boutevin, B.; Gontard, N. Eur Pol J 2001, 37, 1533.
8. Pommet, M.; Redl, A.; Morel, M.-H.; Domenek, S.; Guilbert, S. Macromol Symp 2003, 197, 207.
9. Orliac, O.; Silvestre, F.; Rouilly, A.; Rigal, L. Ind Eng Chem Res 2003, 42, 1674.
10. Orliac, O.; Silvestre, F. Macromol Symp 2003, 197, 193.
11. Orliac, O.; Rouilly, A.; Silvestre, F.; Rigal, L. Ind Crops Prod 2003, 18, 91.
12. Yoshino, T.; Isobe, S.; Maekawa, T. J Am Oil Chem Soc 2002, 79, 345.
13. Wang, Y.; Rakotonirainy, A. M.; Padua, G. W. Starch 2003, 55, 25.
14. Wu, Q.; Sakabe, H.; Isobe, S. Polymer 2003, 44, 3901.
15. di Gioia, L.; Guilbert, S. J Agric Food Chem 1999, 47, 1254.
16. Tillekeratne, M.; Easteal, A. J. Polym Int 2000, 49, 127.
17. Wei, W.; Baianu, I. C. Macromol Symp 1999, 140, 197.
18. di Gioia, L.; Cuq, R.; Guilbert, S. Macromol Symp 1999, 144, 365.
19. Cuq, B.; Gontard, N.; Guilbert, S. Lebensm-Wiss u-Technol 1999, 32, 107.
20. Sothornvit, R.; Olsen, C. W.; McHugh, T. H.; Krochta, J. M. J Food Sci 2003, 68, 1985.
21. McHugh, T. H.; Aujard, J-F.; Krochta, J. M. J Food Sci 1994, 59, 416.
22. Yamauchi, K.; Yamauchi, A.; Kusunoki, T.; Kohda, A.; Konishi, Y. J Biomed Mater Res 1996, 31, 439.
23. Schrooyen, P. M. M.; Dijkstra, P. J.; Oberthur, R. C.; Bantjes, A.; Feijen, J. J Agric Food Chem 2000, 48, 4326.
24. Schrooyen, P. M. M.; Dijkstra, P. J.; Oberthur, R. C.; Bantjes, A.; Feijen, J. J Agric Food Chem 2001 , 49, 221.
25. Vincent, J. Structural Biomaterials; Princeton University Press: Princeton, NJ, 1990.
26. Fraser, R. D. B.; MacRae, T. P.; Rogers, G. E.Keratins: Their Composition, Structure, and Biosynthesis. Charles C. Thomas Publisher: Springfield, Illinois, 1972.
27. Fraser, R. D. B.; MacRae, T. P. In Symposia of the Society for Experimental Biology Number XXXIV: The Mechanical Properties of Biological Materials; Vincent, J. F. V.; Currey, J. D., Eds.; Cambridge University Press: Cambridge, UK, 1980.
28. Arai, K. M.; Takahashi, R.; Yokote, Y.; Akahane, K. Eur J Biochem 1983, 132, 501.
29. Parkinson, G. Chem Eng 1998, 105, 21.
30. Gassner, G.; Schmidt, W.; Line, M. J.; Thomas, C.; Water, R. M. U. S. Patent 5 1998, 705, 030.
31. Schmidt, W. F.; Jayasundera, S. In Natural Fibers Plastics, and Composites-Recent Advances; Wallenberger, F.; Weston, N., Eds. Kluwer Academic Publishers: Norwell, Massachusetts, 2003.
32. Woodin, A. M. Biochem J 1954, 57, 99.
33. Yamauchi, K.; Maniwa, M.; Mori, T. J Biomater Sci Pol Ed 1998, 9, 259.
34. Whitaker, J. R.; Tannenbaum, S. R. Food Proteins. AVI Publishing Co, Inc.: Westport, Connecticut, 1977.
35. Feughelman, M. Mechanical Properties and Structure of Alpha-Keratin Fibres; University of New South Wales Press: Sydney, 1997.
36. Barone, J. R.; Schmidt, W. F. Composites Science and Technology 2005, 65, 173.
37. Purslow, P. P.; Vincent, J. F. V. J Exp Biol 1978, 72, 251.
38. Bonser, R. H. C.; Purslow, P. P. J Exp Biol 1995, 198, 1029.
39. Cameron, G. J.; Wess, T. J.; Bonser, R. H. C. J Struct Biol 2003, 143, 118.
40. Wuthrich, K. NMR of Proteins and Nucleic Acids. Wiley, New York, 1986.
41. Di Gioia, L.; Cuq, B.; Guilbert, S. Int J Biol Macromol 1999, 24, 341.
42. Fox, P. F.; Condon, J. J. Food Proteins; Applied Science Publishers: London, 1982.
43. Odian, G. Principles of Polymerization; John Wiley and Sons: New York, 1991.